

30.03.05

**Europäisches  
Patentamt****European  
Patent Office****Office européen  
des brevets****Bescheinigung****Certificate****Attestation**

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

**Patentanmeldung Nr.    Patent application No.    Demande de brevet n°**

04077106.5

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

R C van Dijk

**BEST AVAILABLE COPY**



Anmeldung Nr:  
Application no.: 04077106.5  
Demande no:

Anmeldetag:  
Date of filing: 20.07.04  
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

DSM IP Assets B.V.  
Het Overloon 1  
6411 TE Heerlen  
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:  
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se referer à la description.)

Oxygen scavenging composition

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)  
revendiquée(s)  
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/  
Classification internationale des brevets:

C08L63/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of  
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL  
PL PT RO SE SI SK TR LI

24335PE

- 1 -

OXYGEN SCAVENGING COMPOSITION

5

The invention relates to an oxygen scavenging composition comprising, a copolymer comprising polypropylene oxide segments and polymer segments and an oxidation catalyst.

Such a composition is known from WO 99/15433. In this document an oxygen scavenging composition is prepared by reactive extrusion of the polymer segments, in particular a polycondensate, and a functionalised polypropylene oxide oligomer. The resulting product, denoted as copolycondensate is applied as such in single layer or multi layer films or is diluted with further polycondensate.

15 It has appeared that this composition has a restricted efficiency in oxygen scavenging properties, making it necessary to apply thicker layers to obtain a certain degree of active oxygen barrier properties.

Aim of the invention is a composition comprising a copolymer comprising polypropylene oxide segments and polymer that shows better active oxygen barrier properties than the known composition.

This is achieved according to the invention in that the copolymer has been prepared by copolymerising the corresponding monomers in the presence of functionalised polypropylene oxide segments.

Surprisingly it has appeared that the fact that the polymer segments have been formed from copolymerisation of the corresponding monomers with functionalised polypropylene oxide segments rather than having these functionalised polypropylene oxide segments react with already polymerised polymer segments causes a considerable difference in oxygen scavenging properties of the composition.

30 The composition according to the invention shows highly advantageous active oxygen scavenging properties.

Polycondensates, also known as condensation polymers, among which polyesters and in particular polyamides, form a certain barrier for oxygen and are for this and other reasons applied as films, wraps, bottles, vessels or other

- 2 -

containers for feed and foods and drinks. They protect the packed goods from direct contact with the environment, including the oxygen in ambient air. Since layers of these polymers are not completely impermeable to oxygen it is known to mix a compound into the polymer that is able to scavenge oxygen permeating  
5 into the polymer layer by a chemical reaction binding the oxygen.

Such compounds are known as active oxygen scavengers. Among these polyalkylene oxides and polydienes have been reported to be examples of active oxygen scavengers. It is also known to apply oxygen scavengers that are reactive with polycondensate and to make the scavenger react with the  
10 polycondensate during the mixing, e.g. by reactive extrusion.

Examples of polycondensates are polyesters and polyamides. Examples of suitable polyesters are polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyethylene naphthanoate (PEN), polybutylene naphthanoate (PBN). Examples of suitable polyamides (PA) are aliphatic polyamides, that  
15 may eventually be branched polyamides, such as PA6, PA4,6, PA6,6, PA 11, PA12, semi aromatic polyamides as MXD6, PA6,1/6,T, PA6,6/6,T, fully aromatic polyamides and copolymers and blends of the listed polyamides and polyesters.

As the oxygen scavenging compound in the composition  
20 according to the invention a copolymer comprising functionalised polypropylene oxide (PPO) segments and polymer segments is used, that has been prepared by polymerising the corresponding monomers of the polymer in the presence of polypropylene oxide segments. This is different than the copolymers known from the prior art that are obtained by reactive extrusion of functionalised PPO  
25 oligomer segments and preformed polymer segments of certain length or molecular weight. In the production process known from WO 99/15433 the PPO oligomer segments usually are functionalized with end groups that can react with reactive sites of the polymer. Examples of such functional end groups and reactive polymer sites are e.g. known from WO 99/15433. The same  
30 functionality may have been applied in the copolymerisation process of the copolymer applied in the present invention.

Suitable PPO segments are linear oligomers of PPO and are preferably of the substituted type. In IUPAC nomenclature this PPO is denoted

- 3 -

as polypropylene glycol (polyoxy-1,2-propanediyl). They consist of 2 to 5000 polypropylene oxide monomer units, preferably of 10 to 2500 units and in this shape and size they have been copolymerised with the monomers. In this range an even distribution of the copolymers in the polycondensate appears to be achieved. During this copolymerisation copolymers of the -ABABA- type are formed comprising polymer segments A of variable length alternated with propylene oxide segments B.

In another embodiment the PPO segments are present as branches in a two, three, four or higher star branched compound the centre unit of which can be e.g. a di-, tri-, tetra or higher functional ester, amide, ether, urethane. In the process of preparation of the copolymer applied in the composition of the invention, the polymer segments then grow from the free ends of the PPO segment branches. During this copolymerisation linear copolymers can be formed of the type ABA or branched copolymers having branches of the type BA.

Apart from the PPO segments also other ether segments optionally may be present as e.g. polyethylene oxide, however in smaller amounts than the PPO. Preferably the other ether segments are present in amounts less than 40 wt%, more preferably less than 30 wt% or less than 10 wt% of the amount of PPO.

Suitable polymer segments in the copolymers that have been formed by copolymerising the corresponding monomers in the presence of the PPO segments are those that form the building monomers for the polycondensates described above, in particular polyesters and aliphatic polyamides, preferably PA6 or PA6,6.

These copolymers can be formed by reacting the functionalised PPO in the presence of the monomers at conditions well known for the polymerisation of the corresponding monomers or according to US 4590243 and EP 0067695.

In these processes, apart from the monomers and the PPO segments, also other compounds can be present, for example catalysts, chain stoppers, stabilisers and the like. Linear PPO segments are introduced in these reactions as divalent moieties that are functionally terminated at their ends, e.g.

- 4 -

with hydroxy, amino or acid or other groups that are capable reacting with the monomers the polymer part is polymerised from. In star branched type PPO segments the free ends, i.e. those ends of the PPO part of the PPO segment that are not bound to the centre moiety of the star, are functionalised with the groups mentioned above.

In copolymers that can be applied in the composition according to the invention the relative amount of the PPO can be within the range of 0.5 to 40 wt%, preferably of 1 to 30 wt%. Lower amounts will diminish in particular the period during which the oxygen scavenging properties will remain at a high level. Higher amounts may lead to the formation of a co-continuous phase of PPO segments in the composition. This is detrimental for the total oxygen barrier capacity of the composition and therefore the amount of PPO in the composition should be taken so that the PPO forms a disperse phase in the composition

The oxygen scavenging PPO segments are advantageously present in the composition as small conglomerates in the composition. These conglomerates may be spherical and having a size, i.e. a diameter or a smallest axis, an axis being defined as a line connecting two diametrically located points on the surface of the conglomerate, of up to 500 nm and preferably at most 30 or more preferably at most 25% of the conglomerates have a diameter or smallest axis above 500 nm. Spherical is to be understood as having the same or nearly the same dimension in the three spatial directions, deviating from a spherical shape to such extent only that the length of an axis, is at most 1.3 times the length of the diameter of a sphere having the same volume. Preferably at least 50% of the conglomerates have a size of at most 300 nm and preferably of at most 200 nm. More preferably at least 70, 90 or even 99 % of the conglomerates is within the specified ranges. A lower conglomerate size has appeared to lead to better oxygen barrier properties.

It was further found that an object, comprising a layer of the composition according to the invention, shows enhanced oxygen scavenging performance when a majority of the conglomerates in their shapes have an aspect ratio and in majority are oriented. Such conglomerates can have an elongated or flattened shape, like a cigar or pancake shape. A conglomerate

- 5 -

having an aspect ratio is characterized by the feature that its dimension in at least one spatial direction is larger than its dimension in at least one other spatial direction. The ratio between said dimensions preferably is at least 1.3 and more preferably at least 2 or even 5 or even 50 or more than 100. This is

5 contrast to conglomerates that have essentially the same dimension in the three spatial directions. Oriented here means that the largest dimension extends in a spatial direction parallel to a surface of the object that is exposed to oxygen to be scavenged. This largest dimension of the conglomerate in said parallel direction may be larger than 500 nm, even up to some millimetres. However,

10 the dimension of the conglomerate perpendicular to said surface preferably is below 400 nm and more preferably below 350 nm. This appears to enhance the transparency of the oxygen-scavenging layer in the object significantly. An object containing conglomerates having an aspect ratio can be obtained by subjecting the object during or after it being manufactured to an orientating step,

15 e.g. by exposing it to shear in a molten state, by pressing and in particular by drawing in one or more directions.

The invention thus also relates to an object, having at least one surface that is to be exposed to an oxygen containing environment, and comprising a layer containing the composition according to the invention in

20 which conglomerates of the PPO segments are present, of which conglomerates at least 50 %, preferably at least 70 % and more preferably at least 90 % have a dimension in at least one spatial direction that is larger than a dimension in at least one other spatial direction by a factor of at least 1.3, and in which said larger dimension extends in a spatial direction parallel to the at least

25 one surface of the object.

The composition according to the invention further comprises an oxidation catalyst, promoting the oxygen scavenging activity of the oxygen scavenging compound.

Suitable oxidation catalysts include transition metal catalysts,

30 which can readily switch between at least two oxidation states. Preferably, the transition metal is in the form of a transition metal salt or transition metal complex, wherein the metal is selected from the groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the periodic system of the elements. Suitable metals include

- 6 -

Manganese II or III, Iron II or III, Chromium II or III, Cobalt II or III, Copper I or II, Nickel II or III, Rhodium II, or II or IV and Ruthenium I, II or IV, Titanium III or IV, Vanadium III, IV or V.

Preferably Co II or III is used as the metal part in the catalyst.

5                    Suitable counterions for the metal include, but are not limited to, chloride, acetate, acetylacetonate, stearate, propionate, palmitate, 2-ethylhexanoate, neodecanoate or naphthenate. The metal may also be an ionomer, in which case a polymeric counter ion is employed. Such ionomers are well known in the art. As an example of a suitable complexing moiety  
10 phthalocyanine is mentioned. The transition metal compounds may be present between 10ppm and 10wt%.

Preferably the amount of transition metal compound in the composition is between 50 and 5000 wt.ppm.

Further the composition according to the invention may  
15 comprise other usual additives that may give a certain additionally required property to the composition, examples of which are fibres, fillers, nano-particles, antioxidants, flame retardants, mould release agents and other compounds known in the art for this purpose.

The composition according to the invention has excellent  
20 oxygen barrier properties, e.g. it has an oxygen barrier lower than 0.3 preferably lower than 0.1 cc.mm/(m<sup>2</sup>-day-atm) when measured according to ASTM standard D3985 under dry conditions on a film having a thickness of 60 µm.

The composition of the invention can be applied as a layer in multi-layer films, preferably as an inner layer, sandwiched between other layers.  
25 In such a sandwich construction the active lifetime and effectiveness of the composition is considerably enhanced in comparison with a layer that is directly exposed to the environment. Further applications are layers in the wall of bottles, vessels or other containers, in particular those applied for packaging of foods or other substances that degrade in quality under the influence of oxygen.  
30 The invention thus further relates to the use of the composition according to the invention for the applications mentioned. Suitable methods for this are known per se and are the commonly used shaping and manufacturing techniques for polymer materials.



- 7 -

The oxygen scavenging composition comprising the copolymer and an oxidation catalyst can be prepared by mixing the copolymer with the oxidation catalyst in a separate step or in a step of manufacturing an object from the composition according to the invention.

5 This mixing can be conducted in the equipment known in the art for mixing thermoplastic polymers such as extruders and mixers. The process applies melt-mixing, i.e. the mixing takes place above the melting point of the oxygen scavenging copolymer but below its decomposition temperature.

The invention will be elucidated by the following examples  
10 without being restricted thereto.

#### Experiment 1: Preparation of oxygen scavenging copolymers

##### 15 Preparation of copolymer 1

A flask equipped with stirrer, thermocouple and nitrogen inlet was charged with caprolactam (88.8 wt% ) and a PPO-containing oligomer (Brüggemann P1-30, polypropyleneglycol ester acyl caprolactam) (11.2 wt%). This mixture was diluted in a 1:1 fashion with a catalyst solution (Brüggemann  
20 C1, 12% caprolactam magnesium bromide in caprolactam). After mixing at 100°C the resulting mixture was poured in a mould and kept for 5 minutes at 145°C. The solid co-polyamide, containing 5 wt% polypropylene glycol, was removed from the mould and ground.

##### 25 Preparation of copolymer 2

A flask equipped with stirrer, thermocouple and nitrogen inlet was charged with caprolactam (55.6 wt% ) and a PPO-containing oligomer (Brüggemann P1-30, polypropyleneglycol ester acyl caprolactam) (44.4 wt%). This mixture was diluted in a 1:1 fashion with a catalyst solution (Brüggemann  
30 C1, 12% caprolactam magnesium bromide in caprolactam). After mixing at 100°C the resulting mixture was poured in a mould and kept for 5 minutes at 145°C. The solid co-polyamide, containing 20 wt% polypropylene glycol, was removed from the mould and ground.

- 8 -

Preparation of copolymer 3 (Comparative)

A flask equipped with stirrer, thermocouple and nitrogen inlet was charged with caprolactam (29.9 wt% ) and a PPO-containing oligomer (Brüggemann P1-30, polypropyleneglycol ester acyl caprolactam) ( 70.1 wt%).

- 5 This mixture was diluted in a 2:1 fashion with a catalyst solution (Brüggemann C1, 15% caprolactam magnesium bromide in caprolactam). After mixing at 100°C the resulting mixture was poured in a mould and kept for 5 minutes at 145°C. The solid co-polyamide, containing 42 wt% polypropylene glycol, was removed from the mould and ground.

10

Preparation of copolymer 4

A 2 L reactor equipped with distillation column and stirrer was charged with 790 g dimethylterephthalate, 560 g 1,4-butane diol, 100 g poly(ethyleneoxide-propyleneoxide-ethyleneoxide), 250 mg of titanium tetrabutoxide and 150 mg of magnesium acetate tetrahydrate. After 3 times having flushed the reactor with nitrogen, the reactor content was heated under stirring and atmospheric pressure gradually within one hour to a temperature of 150°C, kept at this temperature for half an hour, and subsequently further heated within 2 hours to a temperature of 220°C. The thus obtained transesterified product was then further polymerised at 240°C under vacuum (down to 2 mbar) for 150 minutes at a stirring speed of 20 RPM. The polymerised product was released from the reactor, under nitrogen pressure, in the form of a strand, cooled in water and granulated in a pelletiser.

25 Preparation of copolymer 5 (Comparative)

A 2 L reactor equipped with distillation column and stirrer was charged with 800 g dimethylterephthalate, 495 g 1,4-butane diol, 100 g poly(tetrahydrofuran-1000), 480 mg of titanium tetrabutoxide and 300 mg of magnesium acetate tetrahydrate. After 3 times having flushed the reactor with nitrogen, the reactor content was heated under stirring and atmospheric pressure gradually within one hour to a temperature of 150°C, kept at this temperature for half an hour, and subsequently further heated within 2 hours to a temperature of 220°C. The thus obtained transesterified product was then

30

- 9 -

further polymerised at 240°C under vacuum (down to 2 mbar) for 150 minutes at a stirring speed of 20 RPM. The polymerised product was released from the reactor, under nitrogen pressure, in the form of a strand, cooled in water and granulated in a pelletiser.

5

Experiment 2: Preparation of oxygen scavenging samples

Copolymers 1, 2, 3, 4 and 5 were melt-mixed with the oxidation catalyst cobalt acetate. The mixing was carried out at a barrel temperature of 260°C, a rotation speed of 120 rpm and a residence time of 3 minutes. All experiments were carried out under nitrogen atmosphere. The copolymers were dried before processing. The materials prepared were stored in sealed bags after processing. Information regarding these samples is given in Table 1.

For comparison, samples C1 and C2 based on a functionalised PPO oligomer (Jeffamine D-2000 of Huntsman) and polyamide 6 (DSM Akulon F132-E, viscosity number 210 ml/g ISO 307, Relative Viscosity measured in 90% formic acid at 30 °C: 3.20) have been prepared by a reactive extrusion process on the lab-scale twin-screw extruder with residence times of 3 and 5 minutes.

Also a polyamide 6 reference not containing an oxygen scavenging compound was prepared (sample D) serving as a reference for samples 1, 2, A, C1 and C2.

Also a poly butylene terephthalate (DSM Arnite T04 200, Relative Viscosity measured of a 1 wt% solution in m-cresol at 25°C: 1.85) reference sample not containing an oxygen scavenging compound was prepared (sample E) serving as a reference for samples 3 and B, see table 1.

- 10 -

Table 1

Sample	Oxygen scavenging compound	PPO content (wt%)	Co(Ac) <sub>2</sub> content (ppm)
1	Copolymer 1	5	1000
2	Copolymer 2	20	1000
A	Copolymer 3	42	1000
3	Copolymer 4	6.8	1000
B	Copolymer 5	10	1000
C1	Jeffamine* D-2000	4.8	1000
C2**	Jeffamine* D-2000	4.8	1000
D	None	0	1000
E	None	0	1000

\* Amine end-capped PPO of Huntsman

5 \*\*:- residence time 5 minutes

Experiment 3: Preparation of oxygen scavenging films

All samples were ground under cryogenic conditions. The resulting powders were pressed between flat hot plates into films with a thickness in the range 55-75 micrometer. The dimensions of the film were 13\*13 cm<sup>2</sup>. Pressing conditions were: plates temperature: 260°C, time between plates without pressure: 5 min, subsequently pressurizing the system for 3 minutes at 10kN.

15 Experiment 4: Measuring of oxygen permeability of films

The oxygen permeability of the prepared films was measured by a MOCON OX-TRAN 2/21 permeameter according to ASTM D3985 by exposing the films to a nitrogen environment on one side and an oxygen atmosphere at the other side of the films leading to an oxygen partial pressure

- 11 -

difference over the films of 1 bar. The permeability tests were conducted under dry conditions at room temperature (23°C). The measurements were performed after 50 hours conditioning at the measurement conditions.

In Table 2 the oxygen permeability is presented for the various films. The  
5 oxygen permeability is normalised with respect to film thickness.

Table 2

Sample	Oxygen permeability (cc mm/(m <sup>2</sup> day atm))
1	0.0
2	0.0
A	87.34
3	< 0.2
B	4.55
C1	0.46
C2**	0.47
D	1.03
E	14.92

10

The detection limit of the Oxtran permeameter is  $5 \cdot 10^{-3}$  cc/(m<sup>2</sup>.day. atm). For the given thickness range of the samples, this leads to an intrinsic permeability limit of about  $4 \cdot 10^{-4}$  cc.mm/(m<sup>2</sup>.day.atm). The intrinsic oxygen permeability of samples 1 and 2 is smaller than  $4 \cdot 10^{-4}$   
15 cc.mm/(m<sup>2</sup>.day.atm).

A comparison of the oxygen barrier results of the polyamide based oxygen scavenging samples (samples 1, 2, A, C1, C2) and the correspondent reference sample D learns that samples according to the invention, i.e. samples 1 and 2, have oxygen permeability values smaller than  
20  $4 \cdot 10^{-4}$  cc.mm/(m<sup>2</sup>.day.atm) for compositions containing 1000 ppm of oxidation catalyst. These values are much lower than the value for Comparative samples A1 and A2, which were prepared according to the process disclosed in WO

- 12 -

99/15433. The values are also much lower compared to reference sample D. In the case of sample A, the oxygen barrier performance is rather poor due, most probably to the fact that the ether phase becomes co-continuous. In the case of samples 1 and 2 the ether phase is of a disperse nature.

5                   A comparison of the oxygen barrier results of the polyester based oxygen scavenging samples (samples 4, 5) and the correspondent reference sample C learns that the sample according to the invention, i.e. sample 4, has an oxygen permeability values smaller than 0.2 cc.mm/(m<sup>2</sup>.day.atm) for compositions containing 1000 ppm of oxidation catalyst.

10 This value is much lower than the value for sample B containing a tetrahydrofuran based ether system instead of a PPO based ether system proving PPO is superior with respect to oxygen scavenging capability compared to this other ether. The value is also much lower than reference sample E containing no oxygen scavenging component.

15

20

- 13 -

CLAIMS

1. Oxygen scavenging composition comprising a copolymer comprising polypropylene oxide segments and polymer segments and an oxidation catalyst, characterized in that the copolymer has been prepared by copolymerising the corresponding monomers in the presence of functionalised polypropylene oxide segments.
2. Oxygen scavenging composition according to claim 1, wherein the polymer segments are polyamide or polyester.
3. Oxygen scavenging composition according to claim 1 or 2, wherein the amount of polypropylene oxide segments is from 0.5 to 40 wt% with respect to the composition.
4. Oxygen scavenging composition according to claim 4, wherein said amount is in the range from 1 to 30 wt%.
5. Oxygen scavenging composition according to any of claims 1 - 4, wherein the polycondensate is absent and wherein the polypropylene oxide segments are present as spherical conglomerates and at most 25% of the conglomerates have a size above 300 nm.
6. Oxygen scavenging composition according to any of claims 1 to 5, wherein the oxidation catalyst is a transition metal salt or complex.
7. Oxygen scavenging composition according to any of claim 1 - 6, having an oxygen barrier lower than 0.3 cc.mm/(m<sup>2</sup>-day-atm) when measured according to ASTM standard D3985 under dry conditions on a film having a thickness of 60 µm.
8. Oxygen scavenging composition according to claim 7, having an oxygen barrier lower than 0.1 cc.mm/(m<sup>2</sup>-day-atm) when measured according to ASTM standard D3985 under dry conditions on a film having a thickness of 60 µm.
9. Use of the oxygen scavenging composition according to any of claims 1 to 9 for the manufacture of an oxygen-scavenging object.
10. Use according to claim 9, wherein the object is a container for food, drink or feed packaging such as a film, a bottle, a vessel or a wrap.

- 14 -

11. Use according to claim 10, wherein the object is a multilayer object in which a layer of the oxygen scavenging composition is sandwiched between two layers of another material.
12. Object, having at least one surface that is to be exposed to an oxygen containing environment, and comprising a layer containing the composition according to any of claims 1 to 8, in which conglomerates of the polypropylene oxide segments are present, of which conglomerates at least 90% has a dimension in at least one spatial direction that is larger than a dimension in at least one other spatial direction by a factor of at least 1.3, and in which said larger dimension extends in a direction parallel to the at least one surface.
13. Object according to claim 12, wherein the dimension of at most 25% of the conglomerates in a direction perpendicular to the at least one surface is less than 350 nm.
14. Object according to claim 13, wherein the object is a container for food, drink or feed packaging such as a film, a bottle, a vessel or a wrap.
15. Object according to claim 13, wherein the object is a multilayer object in which a layer of the oxygen scavenging composition is sandwiched between two layers of another material.

20



- 15 -

**ABSTRACT**

Oxygen scavenging composition comprising a copolymer comprising polypropylene oxide segments and polymer segments and an  
5 oxidation catalyst, characterized in that the copolymer has been prepared by copolymerising the corresponding monomers in the presence of functionalised polypropylene oxide segments and process for the preparation of this composition.

# Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/NL04/000856

International filing date: 09 December 2004 (09.12.2004)

Document type: Certified copy of priority document

Document details: Country/Office: EP  
Number: 04077106.5  
Filing date: 20 July 2004 (20.07.2004)



Date of receipt at the International Bureau: 25 April 2005 (25.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland  
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☒ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☒ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**